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13. ABSTRACT (Maximum 200 words) Determination of thermodynamic quantities (K , ΔH° , ΔS° , and ΔC_p°) for chemical reactions in the supercritical water region has special requirements. During the grant period, progress has been made in meeting these requirements in several areas. First, a new calorimeter has been constructed that overcomes significant experimental challenges in this temperature region. In this calorimeter, the reaction vessel and associated tubing are immersed in a eutectic-salt bath. This feature and the use of a thermoelectric cooler make it possible to minimize baseline corrections. Second, a novel model based on Helmholtz energy and capable of accounting for ion dissociation has been formulated. This model has been tested on experimental heat of reaction and heat of dilution data and has been shown to be superior to the Anderko-Pitzer equation in accounting for the measured heats in this temperature region. Third, heats of dilution, heats of mixing, and heats of reaction were determined for selected chemical systems and used to verify the achievement of the first and second items. The progress made during the grant period provides information that will be valuable for the design of processes needed for operation under supercritical water conditions.					
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THERMODYNAMIC AND MODELING STUDY OF SELECTED
AQUEOUS CHEMICAL SYSTEMS FROM 370 TO 450
DEGREES CELSIUS

FINAL PROGRESS REPORT

Dr. Reed M. Izatt and Dr. John L. Oscarson

March 30, 2001

U.S. ARMY RESEARCH OFFICE

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I. Final Progress Report

A. Statement of the Problem Studied

Understanding chemical reactions that occur in the water critical region requires a knowledge of the equilibrium constants (K) for solute-solute interactions in aqueous solutions. In addition, the nature of solute-solvent interactions must be understood since the structure and properties of water show large changes in the critical region. The thermodynamic quantities ΔH , ΔS , ΔC_p° give insight into both the solute-solute and solute-solvent interactions.

At temperatures higher than 350°C, existing models do not account for ion dissociation in chemical reactions. In addition, it becomes increasingly difficult to maintain the calorimeter reaction zone at a constant temperature using an air bath assembly. Finally, maintenance of the calorimetric equipment becomes increasingly difficult.

The problems studied and overcome during the Grant period were how to circumvent these difficulties by (1) devising a new calorimeter capable of producing reliable heat data at temperatures above 350°C with minimal equipment breakdown and (2) devising a model based on Helmholtz energy capable of accounting for ion dissociation and producing reliable heat data. Heats of dilution, heats of mixing, and heats of reaction were determined for several chemical systems and were used to verify the achievement of the goals indicated in (1) and (2).

B. Summary of the Most Important Results

Significant progress has been made in overcoming the problems indicated in Section A. The results of our work during the past Grant period are either published or in press. These results are now summarized.

1. New Flow Calorimeter using a Eutectic Molten Salt as the Temperature Control Medium

A new isothermal flow calorimeter for measuring heats of mixing of two fluid streams at high temperatures and pressures has been described (see Section C.1.a). The main advantages of the new calorimeter over earlier ones are simplification of the design making it easier to maintain the equipment, reduction of the temperature gradients so that baseline corrections are minimized, and ability to make reliable measurements above 350°C. Immersion of the reaction vessel and associated tubing in a eutectic-salt bath and the use of a thermoelectric cooler make it possible to maintain the reaction zone at a constant temperature. Energy effects from 2.5 to 2000 mW can be measured to a precision of $\pm 1.5\%$ or ± 0.5 mW, whichever is greater. The relatively high uncertainty is due to the difficulties of operating at temperatures and pressures near and above the critical point of water. The calorimeter was tested by measuring the heat of mixing of sodium chloride solutions and water at 300°C (9.3 MPa), 350°C (17.6 MPa), 370°C (24.6 MPa), and 380°C (24.7 MPa). The results at 300 and 350°C were in good agreement with our earlier results¹ and were within 10% of earlier results by Busey et al.² No data are available in the literature at 370 and 380°C. However, our results at these temperatures appear to be reasonable.

2. New Model Incorporating Ion Dissociation of Sodium Chloride for Use in the Water Critical Region

A new model has been developed (see Section C.1.b) that combines a Helmholtz energy expression developed by Anderko and Pitzer³ valid in the critical region of water with a mathematical equation developed by Wood and coworkers^{4,5} describing the dissociation of aqueous sodium chloride. The new model takes into account the effects of ionic dissociation, hard sphere interactions, and dipole-dipole interactions. The new model and the Anderko-Pitzer model were tested by comparing measured heats of dilution of NaCl in the near critical and supercritical regions of water with those calculated using these models. The heats of dilution of aqueous NaCl solutions calculated using the Anderko-Pitzer model were in poor agreement in the dilute concentration region with those reported by Busey et al.², Chen et al.¹, and with new results reported here. The agreement between experimental heats of dilution and those calculated using the Anderko-Pitzer model depended on the variables solute concentration, temperature, and pressure. This agreement improved as solute concentration or temperature increased or as pressure decreased while the other two variables remained constant. The changes in each case resulted in greater ion association. The incorporation in the present study of a species dissociation term into the Anderko-Pitzer model gave improved results in dilute solutions, at lower temperatures, and at higher pressures where ion association is least.

3. Analysis and Publication of Experimental Results

Calorimetric results have been obtained for several sets of metal-ligand systems. These results are now summarized.

Dilution enthalpies, measured using isothermal flow calorimetry, have been determined (see Section C.1.c) for aqueous solutions of KOH and CsOH at 300°C and 11.0 MPa, 325°C and 14.8 MPa, and for aqueous solutions of NaOH, KOH, and CsOH at 350°C and 17.6 MPa. Previously collected dilution enthalpies for aqueous solutions of NaOH at 300°C and 9.3 MPa and at 325°C and 12.4 MPa were included when fitting the Pitzer parameters. The concentration range of the hydroxide solutions was 0.5–0.02 molal. Parameters for the Pitzer excess Gibbs ion-interaction equation were determined from the fits of the experimental heat data. Equilibrium constants, enthalpy changes, entropy changes, and heat capacity changes for alkali metal ion association with hydroxide ion were estimated from the heat data. For all systems, the enthalpy changes and entropy changes were positive and had accelerating increases with temperature. The resulting equilibrium constants show significant, but smaller, increases with temperature.

Dilution enthalpies, measured using isothermal flow calorimetry, have been determined (see Section C.1.d) for aqueous solutions of BaCl₂ at 300°C and 11.0 MPa, of MgCl₂, CaCl₂ and BaCl₂ at 325°C and 14.8 MPa, and at 350°C and 17.6 MPa. Previously collected dilution enthalpies for aqueous solutions of MgCl₂ and CaCl₂ at 300°C and 10.3 MPa and for aqueous solutions of HCl at 250°C, 275°C, and 300°C at 10.3 MPa and 320°C at 12.8 MPa were included with the new data at 300°C and 11.0 MPa and at 350°C and 17.6 MPa when fitting the Pitzer parameters. The concentration range of the chloride solutions was 0.5 to 0.01 molal. Parameters for the Pitzer excess Gibbs ion-interaction equation were determined from the fits of the experimental heat data. Equilibrium constants, enthalpy changes, entropy changes, and heat

capacity changes for the association of the alkaline earth metal ions and H^+ with chloride ion were estimated from the heat data. For all systems, the enthalpy changes and entropy changes were positive and had accelerating increases with temperature. The resulting equilibrium constants show significant, but smaller, increases with temperature.

Enthalpies of dilution measured using isothermal flow calorimetry have been determined (see Section C.1.e) for aqueous solutions of NaOH, KOH, and HCl at 370°C and 24.6 MPa. Previously collected data at 300, 325, and 350°C were included with the new results when fitting the parameters for the Pitzer excess Gibbs energy ion-interaction equation. Equilibrium constants, enthalpy changes, entropy changes, and heat capacity changes for the association of Na^+ and K^+ with OH^- ion and of H^+ with Cl^- ion were estimated from the heat data. Both enthalpy and entropy changes are positive for all of the systems and increase dramatically as the temperature increases. The resulting equilibrium constants show significant, but smaller, increases with temperature.

C. List of Publications and Technical Reports

1. Papers Published in Peer-reviewed Journals

- a. Fuangswasdi, S.; Oscarson, J.L.; Zhou, L.; Izatt, R.M. "A New Flow Calorimeter Using a Eutectic Molten Salt as the Temperature Control Medium", *Thermochim. Acta*; in press 01/23/01.
- b. Oscarson, J.L.; Palmer, B.A.; Fuangswasdi, S.; Izatt, R.M. "A Novel Model Incorporating Ion Dissociation for Sodium Chloride Solutions Near the Critical Point of Water", *Ind. Eng. Chem. Res.*; in press 02/13/01.
- c. Gillespie, S.E.; Chen, X.; Oscarson, J.L.; Izatt, R.M. "Enthalpies of Dilution of Aqueous Solutions of NaOH, KOH and CsOH at 300, 325, and 350°C"; *J. Solution Chem.*, **1998**, 27, 183-194.
- d. Gillespie, S.E.; Chen, X.; Oscarson, J.L.; Schuck, P.C.; Izatt, R.M. "Enthalpies of Dilution of Aqueous Solutions of HCl, $MgCl_2$, $CaCl_2$, and $BaCl_2$ at 300, 325, and 350 °C"; *J. Solution Chem.*, in press 10/03/00.
- e. Fuangswasdi, S.; Oscarson, J.L.; Zhou, L.; Izatt, R.M. "Enthalpies of Dilution of NaOH, KOH, and HCl and Thermodynamic Quantities for the Formation of the These Species from Their Constituent Ions in Aqueous Solution from 300 to 370 °C", *Ind. Eng. Chem. Res.* **2000**, 39, 3508-3515.

2. Papers Published in Non-Peer-Reviewed Journals or in Conference Proceedings

None

3. Papers Presented at Meetings, but not Published in Conference Proceedings

- a. J.L. Oscarson, S.E. Gillespie, P.C. Schuck, and R.M. Izatt, "Heats of Dilution of $CaCl_2$, $BaCl_2$, and $MgCl_2$ at 300, 325, and 350°C," 52nd Calorimetry Conference, Asilomar, California, August 1997.
- b. J.L. Oscarson, L. Zhou, S. Fuangswasdi, and R.M. Izatt, "New Design for a High-Temperature, High-Pressure Flow Calorimeter," 54th Calorimetry Conference, Tallahassee, Florida, August 1999.

- c. J.L. Oscarson, R.M. Izatt, and B.A. Palmer, "Modified Model for Predicting Heats of Dilution near the Critical Point of Water," 16th IUPAC Conference on Chemical Thermodynamics, Dalhousie University, Halifax, Nova Scotia, Canada, August 2000.

4. Manuscripts Submitted, but not Published

None

5. Technical Reports Submitted to ARO

None

D. List of Participating Scientific Personnel

1. Reed M. Izatt, Principal investigator
2. John L. Oscarson, Co-Principal investigator
3. Saowarux Fuangwasdi, Postdoctoral Associate
4. X.X. Zhang, Postdoctoral Associate
5. Li Zhou, "Design and Construction of a New High-Temperature Calorimeter and Calorimetry Study of Aqueous NaCl, KCl, NaOH, KOH and HCl Solutions at 370 and 380 Degree C," M.S. Thesis, Brigham Young University, December 1999.
6. Bruce Palmer, "An Improved Hemholtz Equation of State Model for Correlating the Properties of Dilute Sodium Chloride Solutions Near the Critical Point of Water," M.S. Thesis, Brigham Young University, August 2000.
7. Paul Schuck, Undergraduate student
8. David Gurlock, Undergraduate student
9. Sue E. Gillespie, Research Technician

E. Report of Inventions

None

F. Bibliography

1. Chen, X.; Oscarson, J.L.; Cao, H.; Gillespie, S.E.; Izatt, R.M. "A New Flow Calorimeter Designed for Operation to 450 °C and 50 MPa"; *Thermochim. Acta*, **1996**, 285, 11-23.
2. Busey, R.H.; Holmes, H.F.; Mesmer, R.E., "The Enthalpy of Dilution of Aqueous Sodium Chloride to 673 K Using a New Heat-flow and Liquid-flow Microcalorimeter. Excess Thermodynamic Properties and Their Pressure Coefficients," *J. Chem. Thermodyn.* **1984**, 16, 343-372.
3. Anderko, A.; Pitzer, K.S., "Equation of State Representation of Phase Equilibria and Volumetric Properties of the System NaCl-H₂O above 573 K," *Geochim. Cosmochim. Acta* **1993**, 57, 1657-1680.
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Solutions of LiCl, NaCl, NaBr and CsBr at 28 MPa and Water Densities from 700 to 260 kg · m⁻³," *J. Phys. Chem.* **1995**, *99*, 11612-11625.

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